^{13}C NMR Analysis of Mixed Carbon Dioxide and Nitrogen Hydrate for Studying the Guest Molecular Dynamics in Hydrate Cages

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Abstract

In this contribution the X-ray diffraction and ^{13}C NMR spectroscopy were used to identify structure and guest distribution of the mixed N_2+CO_2 hydrates. X-ray diffraction results of the mixed N_2+CO_2 hydrates confirmed that the unit cell parameter was ~11.8 Å over the gas mixture composition range of 3 to 20 mol% CO_2 and the formed hydrates were identified as structure I. When the composition of gas mixture was reduced to 1 mol% CO_2, the structure of mixed hydrate was transformed to structure II showing the unit cell parameter of 17.26 Å. The ^{13}C cross-polarization (CP) NMR spectroscopy was used to examine the distribution of carbon dioxide molecules in small 5^{12} and large $5^{12}6^2$ cages of structure I. From NMR spectra of the mixed N_2+CO_2 hydrate formed from gas mixture of 20 and 10 mol% CO_2, the powder patterns having the chemical shift anisotropy of -54.5 and -53.8 ppm were observed, respectively. There was no isotropic line indicating carbon dioxide molecules in the small 5^{12} cages of structure I. These NMR spectra allowed that the carbon dioxide molecules occupied only the large $5^{12}6^2$ cages of structure I when the mixed N_2+CO_2 hydrates was formed at vapor phase composition range of $10 - 20$ mol% CO_2. In addition, from the analysis of the gases collected from dissociating hydrate sample, the amounts of carbon dioxide in mixed N_2+CO_2 hydrates increased greatly with a small increase of carbon dioxide in vapor phase. This result implies that both small and large cages of structure I were likely to prefer to be stabilized by carbon dioxide molecules, resulting the accumulation of gas mixture with high carbon dioxide composition into hydrate phase.

Introduction
Gas hydrates are a general class of crystalline compounds formed by the physically stable interaction between water and relatively small guest molecules.[1] Under suitable conditions of temperature and pressure, water molecules are connected by hydrogen bonding and form into polyhedral cages. The low molecular-weight gas molecules such as methane, carbon dioxide, and nitrogen could be encaged into these cages. Although gas guest molecules are physically enclosed within the cages, no actual chemical union exists between the guest and host water molecules. These non-stochiometric crystalline compounds are divided into three distinct structures I, II, and H, which differ in cavity size and shape.[2] Besides these three structures, a more complex structure that contains two cages of unusual geometry, known as structure T, was also newly observed in the presence of dimethyl ether.[3] It is clear that many of the physical attributes of gas hydrates remain unknown and thus have to be identified in more detail.

Gas hydrate are of particular interest in energy and environmental field because of emerging possible application of hydrate nature to storage of natural gas[4], sequestration of carbon dioxide on the ocean floor[5], and separation of greenhouse gas from flue gas.[6] The literature contains a number of either experimental or theoretical works to understand macroscopic phase behavior and structural characteristics[7-11] of pure and mixed hydrates. However, only a few studies have been conducted concerning the mixture of carbon dioxide and nitrogen in spite of its industrial importance on greenhouse gas separation. Kang et al.[6] developed the basic concept for separating carbon dioxide from power plant flue gas using the mixed hydrate formation of nitrogen and carbon dioxide. They measured hydrate equilibrium conditions of the mixed hydrates and analyzed hydrate phase compositions to verify the feasibility of hydrate-based gas separation process. However, they didn't provide any precise experimental results indicating the structure of mixed hydrate and distribution of guest molecules in hydrate cages. Thus, in the present study, the X-ray diffraction was used to confirm the structure of mixed N_2+CO_2 hydrates and the NMR spectroscopy to identify the distribution of carbon dioxide in both small and large hydrate cages. In addition, the corresponding hydrate-phase compositions were also measured as a macroscopic approach in order to complement the NMR spectroscopic results.

Experimental Section
The X-ray powder diffraction pattern was recorded at 113 K on a Rigaku Geigerflex goniometer diffractometer, using graphite monochromatized Cu Kα radiation (λ=1.5406 Å) in the $\theta/2\theta$ scan mode. Samples were scanned over a range $10^o < 2\theta < 60^o$, with a scan speed of 0.5^o per minute at an increment of 0.05^o in 2θ, giving a total acquisition time for each sample of approximately 2 hr.

The ^{13}C cross-polarization (CP) NMR spectra were recorded on a Bruker DSX 400 NMR spectrometer at a Larmor frequency of 100.6 MHz. The powder samples were placed in a 4 mm o.d. Zirconia rotor loaded into variable temperature probe. The pulse length for proton was 5 μs and pulse repetition delay of 3 s was employed when the contact time of 1.0 ms was used. The down-field carbon resonance peak of adamantane, assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference. The hydrate samples were prepared in a mechanically stirred reactor and formed from finely powdered ice particles that were crushed in a mortar and pestle. The reactor maintained at a constant temperature of 272.1 K was filled with powdered ice

particles and then pressurized with a gas mixture to a higher pressure than the corresponding three-phase equilibrium pressure at the same temperature. Mechanical stirrer agitated the ice particles during the entire formation process to provide the fresh surface to participate in the formation of gas hydrate. After completing the formation process, the mixed hydrate was sampled and transported to Zr-rotor, which was inserted to the pre-cooled NMR probe.

The hydrate compositions were measured by analyzing the gases encaged in the hydrate structures. After the hydrate formation process reached a steady state, the vapor phase was vented to atmospheric pressure at 272.1 K by opening a valve used to isolate the system from the atmosphere. The hydrate was dissociated and the evolving gases were analyzed using the gas chromatograph directly attached to the system.

Results and Discussion

CO_2 dynamics in hydrate cages The X-ray diffraction was adopted as one of the fundamental approaches to determine the crystal structure of gas hydrates. The guest dynamics in hydrate cages was determined by the NMR spectroscopic analysis of hydrate samples. It becomes indispensable to establish the mutual consistency between the structure by X-ray diffraction and the dynamics by NMR spectroscopy in order to obtain the structural characteristics of pure and mixed hydrates. Therefore, for the preliminary reference, these two powerful methods were used to analyze polycrystalline samples of pure CO_2 hydrates, which provides the unit cell parameters and more importantly the guest dynamics of carbon dioxide molecules in small and large cages of structure I.

Figure 1 (a) represents the X-ray diffraction pattern of pure CO_2 hydrate at 113 K, which was known to form structure I, along with the calculated angles of structure I. All the diffraction lines of pure CO_2 hydrate were attributed to structure I and assigned as miller indices at corresponding angles.[12] It is noted that the (110), (200), (210), and (211) diffraction peaks appearing at low angle range showed weak relative intensities comparing with other peaks appeared from 25° to 60°. From these miller indices and 2θ values, the unit cell parameter for polycrystalline sample of pure CO_2 hydrates formed structure I was 11.89 Å. With the results of other structure I samples, all the values were compared and confirmed to be in good agreement.[13,14]

The knowledge of molecular dynamics in small and large cages of structure I could be obtained from analysis of ^{13}C NMR spectral shape of pure CO_2 hydrate. If carbon dioxide molecules were isolated, it shows no chemical shift anisotropy and therefore gaseous carbon dioxide molecules contribute at the isotropic shift. For carbon dioxide enclathrated into hydrate cages, a chemical shift anisotropy have been induced by asymmetry in the immediate environment of the molecules making it a very sensitive probe of guest distribution in hydrate cages.[15] The ^{13}C CP NMR spectrum of pure CO_2 hydrate is shown in Figure 1 (b). Since the small 5^{12} cages of structure I produced pseudo-spherical symmetry so that the molecular motions are isotropic, only a sharp line at the isotropic chemical shift of 123.1 ppm was observed. For carbon dioxide in the large $5^{12}6^2$ cages of structure I, the powder pattern was observed due to asymmetric shape of $5^{12}6^2$ cages and reflected the anisotropic motions of carbon dioxide molecules. The chemical shift anisotropy could be defined as $\Delta = \delta_{iso} - \delta_{zz}$[15], where δ_{iso} is the isotropic chemical shift and δ_{zz} is the zz component of the chemical shift tensor, then the observed chemical shift anisotropy value was –55.3 ppm. The symmetry of

small 5^{12} and large $5^{12}6^4$ cages of structure II were contrary to that of structure I cages. The mixed $CO_2+C_3H_8$ hydrate formed from 80 mol% CO_2 and balanced propane gas mixture was shown in Figure 2, from which the mixed $CO_2+C_3H_8$ hydrate was identified as structure II.[1] Although the carbon dioxide spectrum in Figure 2 is similar to the spectrum observed for structure I, there are clear differences in chemical shift data. The isotropic line observed at chemical shift of 124.6 ppm indicates that carbon dioxide molecules occupy the pseudo-spherical large $5^{12}6^4$ cages. The powder pattern was associated with carbon dioxide molecules in small 5^{12} asymmetric cages and the observed chemical shift anisotropy was –42.2 ppm, slightly different from that of large cages of structure I. The two propane ^{13}C resonance lines are not resolved and observed as a single peak at 16.8 ppm. The ^{13}C NMR spectra shown in Figure 1 and 2 clearly suggest that the cage symmetry could be used as an effective indicator for determining the guest distribution in hydrate cages. Thus, with cross-exploration of X-ray diffraction and ^{13}C CP NMR spectra, it becomes possible to elucidate the structure and guest distribution of mixed hydrates containing carbon dioxide.

Structure and guest distribution of the mixed N_2+CO_2 hydrates It has been known that nitrogen is one of smallest gas hydrate formers when existing as a single guest. Davidson et al.[16] suggested that nitrogen stabilized small cages of structure II and also occupied all of the large cages, while carbon dioxide forms structure I. Only judging from the relative size difference between carbon dioxide molecule and a small cage of structure I, the small cages might remain essentially unoccupied. However, recent studies revealed that carbon dioxide molecules occupied both small and large cages of structure I, in which the large cages were fully occupied and the small cages partially occupied at the portion of 0.71.[14,15] Therefore, when the mixed N_2+CO_2 hydrate forms, carbon dioxide and nitrogen molecules compete each other for better occupancy into the hydrate cages and the resulting structure of mixed hydrate was determined from guest distribution in hydrate cages. In this study, the mixed N_2+CO_2 hydrates were formed from various compositions, the structure and guest distribution were checked through cross examinations of X-ray diffraction and NMR spectroscopy.

First, the mixed N_2+CO_2 hydrates were formed at specific compositions of gas mixture according to flue gas type of power plant. The flue gas usually consists of 10 to 20 mol% CO_2, 5 to 9 mol% O_2, trace gases, and balance N_2. After pretreatment steps, the flue gas might be simplified as the binary mixture of carbon dioxide and nitrogen. For this study to be more practically meaningful and feasible, two gas mixture compositions of 10 and 20 mol% CO_2 were specially chosen to acquire their fundamental structure and guest distribution information. Accordingly, at first, the mixed hydrate was formed from 20 mol% CO_2 and balanced N_2 gas mixture. The obtained X-ray diffraction was shown in Figure 3 (a), which shows good agreement with that of pure CO_2 hydrate in overall range of 2θ values. All the diffraction lines of the mixed N_2+CO_2 hydrates were attributed to structure I and the assigned miller indices at the corresponding angles were similar to those of pure CO_2 hydrate. The unit cell parameter of the cubic cell was 11.83 Å, which suggested that the lattice structure of mixed hydrate was slightly compressed than that of pure CO_2 hydrate due to the relatively high pressure formation condition. The distribution of carbon dioxide molecules in hydrate cages was represented by the ^{13}C NMR spectrum as shown in Figure 3 (b). The powder pattern having the chemical shift anisotropy of –54.5 ppm was only observed and no isotropic line was obtained. Both X-ray diffraction and ^{13}C NMR spectrum indicate that the

structure I forms from 20 mol% CO_2 gas mixture and carbon dioxide molecules were only occupied in the large cages, while nitrogen molecules occupied the small and remaining large cages. Subsequently, the mixed N_2+CO_2 hydrate was formed at 10 mol% CO_2 and balanced N_2 gas mixture. As can be seen in Figure 4 (a), the obtained X-ray diffraction represents that the formed mixed N_2+CO_2 hydrate was structure I. The miller indices of diffraction lines were similar to that of mixed N_2+CO_2 hydrate formed from 20 mol% CO_2 gas mixture and resulting unit cell parameter was identical with the value of 11.83 Å. From the X-ray diffraction results it is known that the mixed hydrates of structure I only form from the binary carbon dioxide and nitrogen gas mixture composition range of 10 to 20 mol% CO_2. The ^{13}C NMR spectrum was shown in Figure 4 (b). The powder pattern having the chemical shift anisotropy of –53.8 ppm was obtained for the mixed N_2+CO_2 hydrate formed from 10 mol% CO_2 gas mixture, indicating that carbon dioxide molecules occupied only large cages as discussed in Figure 3 (b). The $^{13}CO_2$ chemical shift data for different hydrate cages were summarized in Table 1.

At this moment, it remains still unsolved whether the structure II mixed hydrates should be formed from gas mixtures of carbon dioxide and nitrogen. The careful X-ray diffraction analysis was carried out at lower compositions of 6 and 3 mol% CO_2. The resulting diffraction patterns indicated that the mixed hydrates formed structure I showing the unit cell parameters of 11.81 and 11.78 Å, respectively. However, in case of 1 mol% CO_2 gas mixture, the structure II hydrates eventually formed showing the unit cell parameter of 17.26 Å under the conditions of our experiments. These results might suggest that the stabilization of hydrate cages is mainly governed by carbon dioxide molecules occupying the large cage of structure I at compositions above 3 mol% CO_2. It must be however noted that below 1 mol% CO_2 the structure II hydrate was formed and stabilized by nitrogen molecules.

The previous microscopic approaches for hydrate phase analysis using X-ray diffraction and NMR spectroscopy provide valuable information of hydrate structure and carbon dioxide distribution in hydrate cages. But, the exact compositions of carbon dioxide and nitrogen occupying the hydrate cages couldn't be obtained because of the real difficulty for simultaneously analyzing individual molecular distributions of carbon dioxide and nitrogen directly from NMR spectra. Apparently, the macroscopic approach must be introduced to determine the guest compositions in hydrate cages. Thus, the compositions of gases collected from the dissociating hydrate samples were analyzed in order to determine the relative amount of carbon dioxide and nitrogen occupying the hydrate cages. Table 2 lists the resulting carbon dioxide compositions of hydrate phase at the corresponding compositions of vapor phase and, as can be expected, shows a trend of increasing carbon dioxide amount with increasing the composition of carbon dioxide in vapor phase. At low carbon dioxide composition in vapor phase of 1.2 mol% CO_2, the amount of carbon dioxide occupying the hydrate cages appeared to be 9.0 mol% CO_2. Accordingly, nitrogen molecules might be expected to occupy most of small and large cages, while carbon dioxide molecules occupy only the small amount of large cages. However, the amount of CO_2 in hydrate phase greatly increased by changing hydrate structure from II to I above 3 mol% CO_2 in vapor phase as listed in Table 2.

The cross evaluations of macro- and micro- results obtained from the X-ray diffraction, NMR spectra, and hydrate phase compositions make the specific analysis of guest distribution in hydrate cages to be possible. From the X-ray diffraction analysis, the

mixed N_2+CO_2 hydrate was identified to form structure I at compositions above 3 mol% CO_2 in the vapor phase. If we consider the ideal occupation of nitrogen and carbon dioxide molecules in small and large cages respectively, $2N_2 \cdot 6CO_2 \cdot 46H_2O$, then the resulting composition of hydrate phase becomes 75.0 mol% CO_2. However, the obtained hydrate phase compositions varied from 14.6 to 96.5 mol% CO_2 at corresponding composition of vapor phase, indicating that the distribution of carbon dioxide molecules in hydrate cages showed more complex behavior.

Recently, considerable research works regarding the hydrate structure, particularly in case of multi-guests, have been reported, but most of them mainly focused on structural types of the formed hydrates without addressing the guest participation in cages both qualitatively and quantitatively. In fact, the complete analysis of cage occupancy characteristics seem to be very difficult at the present stage even for the mixed hydrates involving only two guests, but the more advanced analytical techniques might help resolving these problems. As a part of contribution, the present research was attempted to explore the structure and guest distribution of the mixed N_2+CO_2 hydrate through X-ray powder diffraction and NMR spectroscopy analysis along with hydrate phase composition measurements.

Conclusions

In this study we focused to identify the structure and guest distribution of mixed N_2+CO_2 hydrate at various compositions of gas mixtures. The crystal structure of mixed hydrates was identified as structure I from the resulting X-ray diffraction pattern at the gas mixture composition range of 3 and 20 mol% CO_2, while the structure of mixed hydrate seemed to be transformed to structure II when the gas mixture composition was reduced to 1 mol% CO_2. On the basis of ^{13}C CP NMR spectra for carbon dioxide, it was demonstrated that only the large cages of structure I were occupied by carbon dioxide molecules. There was no isotropic line indicating the carbon dioxide molecules in small cages of structure I. The analysis of the gases collected from dissociating hydrate samples provides the exact composition of carbon dioxide in hydrate phase. The cross exploration of X-ray diffraction, NMR spectroscopy, and hydrate phase composition analysis suggest that once the mixed hydrate was formed at higher gas mixture compositions than 3 mol% CO_2, the hydrate cages were mainly dominated by carbon dioxide molecules and the overall structure was determined to be structure I. The analysis of the gases collected from dissociating hydrate samples complement the NMR spectroscopic analysis and provides the carbon dioxide distribution in hydrate cages from the facts that the amount of carbon dioxide in mixed N_2+CO_2 hydrates increased greatly with a small increase of carbon dioxide in vapor phase. As increasing the amount of carbon dioxide in vapor phase, the role of stabilizing both small and large cages was transformed from nitrogen to carbon dioxide molecules, which is likely to prefer to stabilize the small and large cages of structure I.

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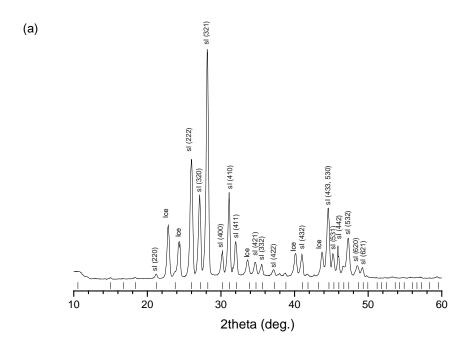Table 1. $^{13}CO_2$ Chemical shift data of pure and mixed hydrates.

System	Hydrate structure	Cage type	$\delta^{iso}(ppm)$	$\Delta(ppm)$
Pure CO_2	Structure I	5^{12}	123.1	0
		$5^{12}6^2$	127.7	- 55.3
$CO_2+C_3H_8$ (80mol% CO_2)	Structure II	5^{12}	128.3	- 42.2
		$5^{12}6^4$	124.6	0
N_2+CO_2 (20mol% CO_2)	Structure I	$5^{12}6^2$	127.6	- 54.5
N_2+CO_2 (10mol% CO_2)	Structure I	$5^{12}6^2$	127.3	- 53.8

Table 2. Hydrate phase compositions of the mixed N_2+CO_2 hydrates measured at the corresponding vapor phase compositions.

Formation condition (K, bar)	Vapor phase composition (mol% of CO_2)	Hydrate phase composition (mol% of CO_2)
272.1, 145	1.2	9.0
272.1, 130	3.3	14.6
272.1, 105	9.9	46.5
272.1, 77	18.4	58.8
272.1, 50	33.3	73.4
272.1, 41	49.9	85.9
272.1, 35	66.5	93.9
272.1, 32	84.7	96.5

Figure captions

Figure 1. (a) X-ray diffraction of the pure CO_2 hydrate forming structure I. (b) ^{13}C CP NMR spectrum of pure CO_2 hydrate at 243K.

Figure 2. (a) ^{13}C CP NMR spectra of the mixed $CO_2+C_3H_8$ hydrate formed from 80 mol% CO_2 and balanced C_3H_8 gas mixture.

Figure 3. (a) X-ray diffraction of mixed N_2+CO_2 hydrate formed from 20 mol% CO_2 and balanced N_2. (b) ^{13}C CP NMR spectra of mixed N_2+CO_2 hydrate formed from 20 mol% CO_2 and balanced N_2.
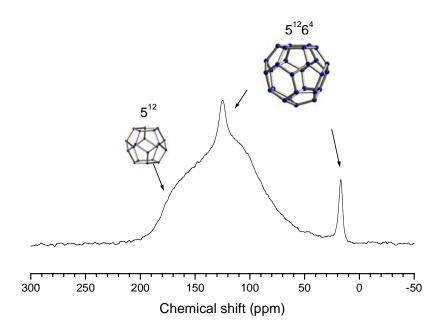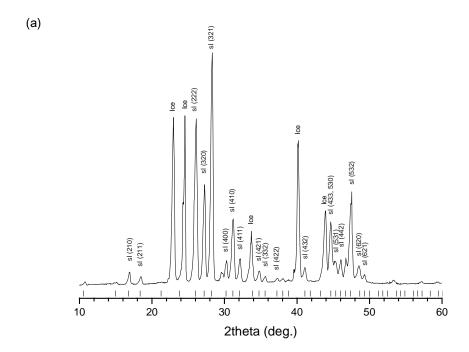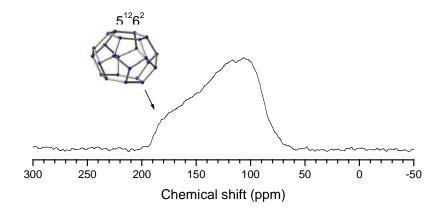
Figure 4. (a) X-ray diffraction of mixed N_2+CO_2 hydrate formed from 10 mol% CO_2 and balanced N_2. (b) ^{13}C CP NMR spectra of mixed N_2+CO_2 hydrate formed from 10 mol% CO_2 and balanced N_2.

(a)

(b)

Figure 1.

Figure 2.

(a)

(b)

$5^{12}6^2$

Figure 3.

(a)

(b)

$5^{12}6^2$

Figure 4.